

On the relaxation dynamics of glass-forming systems: Insights from computer simulations

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Abstract. We discuss the relaxation dynamics of a simple lattice gas model for glass-forming systems and show that with increasing density of particles this dynamics slows down very quickly. By monitoring the trajectory of tagged particles we find that their motion is very heterogeneous in space and time, leading to regions in space in which there is a fast dynamics and others in which it is slow. We determine how the geometric properties of these quickly relaxing regions depend on density and time. Motivated by this heterogeneous hopping dynamics, we use a simple model, a variant of a continuous time random walk, to characterize the relaxation dynamics. In particular we find from this model that for large displacements the self part of the van Hove function shows an exponential tail, in agreement with recent findings from experiments and simulations of glass-forming systems.

Keywords: glass transition; lattice gas; dynamical heterogeneities; computer simulations

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INTRODUCTION

Matter occurs in three different phases: Gas, crystal, and liquid. In a gas the particles are separated by distances that are large with respect to the size of the particles (or more precisely with respect to the typical length-scale for the interaction between the particles). Therefore density is a small parameter which allows an accurate theoretical description of the structure and dynamics of these systems. In a crystal the long range structural order permits to use periodic functions in space and time to describe the lattice vibrations (phonons) of the system and thus we have a quite accurate understanding of the structural, dynamical and mechanical properties of crystals. Things are more difficult in liquids: Their density is comparable to the ones of crystals and hence cannot be used as small parameter. Their structure is neither completely disordered as in a gas nor ordered as in a crystal. Therefore the investigation of structural and dynamical properties of liquids remains an active field of research, despite the knowledge that we have on these systems [1, 2]. One of the most puzzling behavior of liquids is the temperature dependence of their viscosity η . In Fig. 1 we show $\log(\eta)$ for a wide variety of liquids as a function of $1/T$. Note that in this representation an Arrhenius dependence, $\eta(T) \propto \exp(E/k_B T)$ (with E the activation energy and k_B the Boltzmann constant), would just be a straight line. Several important conclusions can be drawn from this graph: 1) The T -dependence of the viscosity is extremely steep in that a change of T by a factor of 2-3 can lead to an increase of η by 12-15 decades. 2)

This T –dependence is non-Arrhenius in that most of the curves are bent upwards, i.e. η shows a super-Arrhenius behavior. 3) The curves show a completely smooth T –dependence. In particular one does not see any discontinuity around the melting temperature of the material. (We note that for most of these liquids the melting occurs at temperatures at which $\eta(T)$ is on the order of $10^0 - 10^4$ Pa s.) Furthermore we mention that for many liquids there is no experimental data for the viscosity for temperatures that are significantly below the melting temperature, since these systems crystallize if they are supercooled. However, as the figure shows, there is indeed a large class of liquids, the so-called “glass-formers” for which the crystallization process is so slow that η can be measured.

Finally we note that the T –dependence of η seems to extrapolate smoothly to even lower temperatures. In view of the experimental fact that the structural relaxation time of a liquid, as measured, e.g., by means of the intermediate scattering function [2], shows a T –dependence that is very similar to the one of η , one thus can conclude that there will be a temperature below which the relaxation time becomes so large that the sample will no longer flow on human time scales, i.e. it has become a *glass*. Despite large efforts to identify the mechanism(s?) that are responsible for the dramatic slowing down of the dynamics of these liquids, and hence of the resulting glass-transition, there is presently no theory that is able to give a reliable description of this dynamics [4, 5, 6, 7, 8].

The strong increase of the viscosity (or the relaxation times) is not the only puzzling feature of glass-forming liquids. If one investigates these systems on a more microscopic scale, e.g. by using light or neutron scattering techniques, one finds that typical time correlation functions, $\phi(t)$, are not given by a Debye-law, i.e. an exponential decay in time, but are instead stretched, i.e. $\phi(t) \propto \exp(-(t/\tau)^\beta)$, with a stretching exponent $\beta < 1.0$ [8, 9]. One possibility to explain this stretching phenomenon is the presence of the so-called “dynamical heterogeneities” [10, 11, 12, 13] in the glass-formers. What do we mean by this? Since the system is disordered, each particle will have a somewhat different environment. Hence it can be expected that each particle has a somewhat

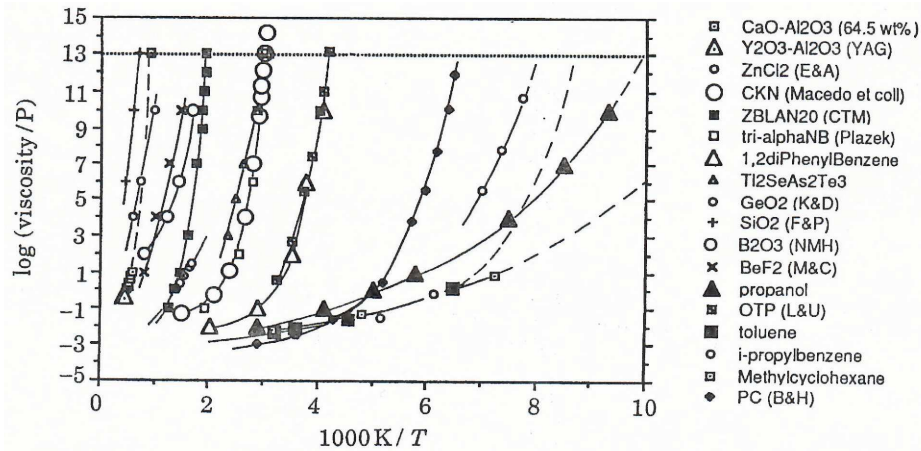


FIGURE 1. Arrhenius plot of the temperature dependence of the viscosity of various glass-forming liquids. After Ref [3].

different relaxation dynamics. Some of them relax faster, some of them slower. This is the qualitative meaning of dynamical heterogeneity. (Of course on the long run the environment of a particle will change and hence a particle that relaxes quickly will become slow and vice versa, i.e. at very large times all particles will have the same statistical properties.) Since in most experiments one is only able to measure the *average* relaxation dynamics of the particles, one will average over (momentarily) fast and slow particles and hence the average time correlation function is not a single exponential, but a superposition of exponentials with different relaxation times, and such an average can usually be described well by a stretched exponential. (The exact form of $\phi(t)$ will depend on its exact nature and on the distribution of fast and slow particles.) Experiments and simulations have shown that these dynamical heterogeneities do indeed exist in that there are regions in the sample in which the particles move quickly and others in which they move slowly [12, 13, 14, 15, 16, 17, 18].

Despite this success to rationalize, at least qualitatively, the stretching, it is presently not very clear to what extent these dynamical heterogeneities are really responsible for understanding the relaxation dynamics of glass-forming liquids [18]. Similarly, the nature of the motion of the particles in the mobile/immobile regions is not well understood. In order to find answers to these questions we have done computer simulations of various glass-forming systems and in the following we will discuss some of the results that have helped to clarify matters at least to some extent. In the first part of this brief review we will discuss the results obtained for a simple lattice gas in which we were able to characterize the nature of the dynamical heterogeneities in great detail. In the second part we will show that the presence of these dynamical heterogeneities have a surprising consequence for certain time correlation functions and will present a simple model, the continuous time random walk, that is able to capture some essential features of these correlation functions.

MODEL AND DETAILS OF THE SIMULATIONS

As discussed in the previous section, the relaxation dynamics of glass-forming systems spans at least 12-15 decades in time. Despite the availability of supercomputers, it is currently impossible to do computer simulations of, say, a system of $O(10^3)$ particles, which extend over that many decades in time. Therefore one has to restrict oneself to a smaller time window and in addition to use interaction potentials that are as simple as possible in order to maximize numerical efficiency. One class of models that has been found to be very useful for the study of glassy dynamics are the so-called lattice gases (or kinetic Ising models) in which the particles (or defects) move on a regular lattice (see Ref. [19] for a review on these systems).

In the present work we will use one particular case of such a lattice gas, the so-called KA model [20] which is defined as follows: N particles populate a cubic lattice of size L^3 with the constraint that a lattice site can be occupied by only one particle. All possible configurations have the same energy and thus the same Boltzmann weight. This property implies that the system does not require equilibration since every randomly generated configuration has the same statistical probability, a feature which is most useful for computer simulations. The imposed stochastic dynamics consists of the following process:

A randomly selected particle can move to any one of the neighboring empty lattice site provided it has m or fewer occupied nearest neighbor sites and that the target empty site has $m + 1$ or fewer occupied nearest neighbor sites. A choice of $m = 3$ results in a dynamics that, at high densities $\rho = N/L^3$, shares many properties of real glass-forming systems, such as stretching of the time correlation functions, dynamical heterogeneities, etc. [20, 21, 22, 23, 24, 25, 26].

For efficient sampling of the configuration space at high densities, we have carried out event-driven Monte Carlo [20, 27] simulations of the model. In the following we will report the results using the lattice spacing as a unit of length and one Monte Carlo sweep of the system as the unit of time. Using periodic boundary conditions, we have investigated system sizes $L = 20, 30$, and 50 , which avoid effects due to finite size [20], with densities spanning from $\rho = 0.65$ to $\rho = 0.89$.

RESULTS

In this section we will discuss the relaxation dynamics of the KA-model. Firstly we will show that this dynamics is indeed quite similar to the one found in more standard (off-lattice) glass-formers. Subsequently we will discuss the dynamical heterogeneities and show how they are related to the relaxation dynamics.

As mentioned above, in this model all possible configurations of particles have the same statistical weight. Therefore the static structure is trivial and shows no relevant ρ -dependence, i.e. in the thermodynamic limit structural quantities like the radial distribution function etc. will depend only on $\rho^{1/3}$. Therefore we can concentrate in the following on the ρ -dependence of the dynamical quantities. One important quantity is the so-called intermediate scattering function $F_s(q, t)$ which is defined as [2]

$$F_s(q, t) = \frac{1}{N} \sum_{j=1}^N \langle \exp(i\vec{q} \cdot (\vec{r}_j(t) - \vec{r}_j(0))) \rangle \quad . \quad (1)$$

Here $\vec{r}_j(t)$ is the position of particle j at time t , \vec{q} is a wave-vector, and $\langle \cdot \rangle$ is the average over the configurations. (Note that due to rotational symmetry, the left hand side depends only on $q = |\vec{q}|$.)

In Fig. 2 we show the time dependence of $F_s(q, t)$ for different densities ρ . The wave vector is $q = \pi$, i.e. one measures the displacement of the particles over a distance which is on the order of one lattice spacing. (Other wave-vectors show a similar t and ρ -dependence.) From this figure we recognize that at low densities the relaxation dynamics is very fast in that the time correlation function decays to zero within 10 Monte Carlo steps (MCS). With increasing ρ the dynamics slows down considerably and at $\rho = 0.86$ it takes more than 10^7 MCS before $F_s(q, t)$ has decayed to zero. Furthermore we note that at the highest densities the shape of the correlator is no longer an exponential, but instead can be fitted well by a stretched exponential with a stretching exponent β around 0.63 [20]. Accompanied with this slowing down is a quick decrease of the diffusion constant for the particles (which can, e.g., be calculated from the mean squared displacement and the Einstein relation) [20]. Hence these results show that, despite its

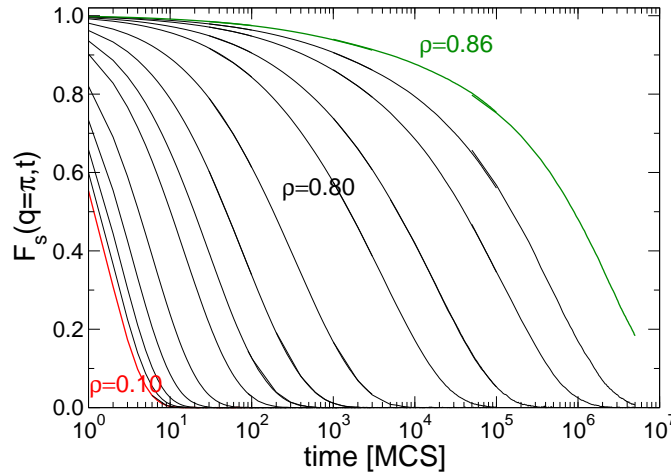


FIGURE 2. Time dependence of the incoherent intermediate scattering function for different densities ρ . From left to right: $\rho = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.65, 0.7, 0.75, 0.8, 0.82, 0.84, 0.85, 0.86$.

simplicity, this lattice gas model shows some of the typical features of glass-forming systems.

How do the particles explore space? In order to find an answer to this question we show in Fig. 3 the trajectory of one tagged particle. The time span is 10^7 MCS and the density is $\rho = 0.87$. As we can recognize from the figure the trajectory consists of relatively compact blobs, having a typical diameter of 6, that are connected by means of narrow pathways. Note that this structure is very different from the one expected for a simple random walk trajectory on a lattice for which, in three dimensions, the walk does not form such compact regions. Thus the particle explores a first blob, finds one of the pathways that leads to a neighboring blob, explores that one, moves on, etc. Thus we can conclude that there is a microscopic mechanism in the system that makes the relaxation dynamics very heterogeneous, i.e. non-uniform in space, and below we will discuss this

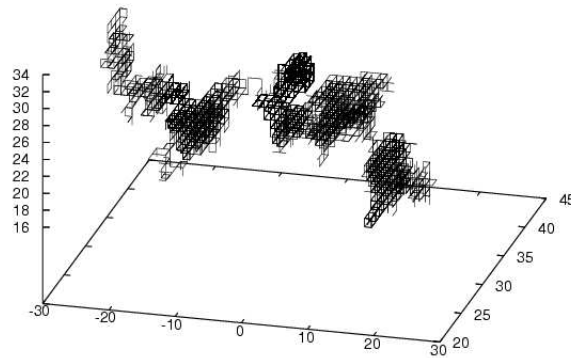


FIGURE 3. Typical trajectory of a tagged particle that is mobile. Total length of the time is 10^7 MCS and the density is $\rho = 0.87$.

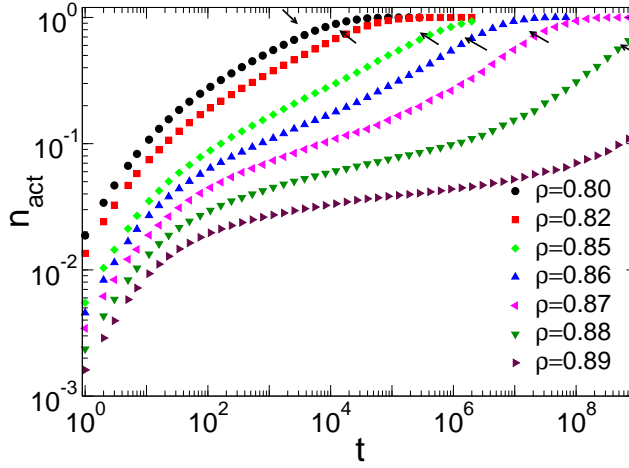


FIGURE 4. Time dependence of the concentration of active sites for different densities. The arrows mark the α -relaxation time τ_α .

point in more detail.

The fact that the tagged particle is able to explore the observed blobs implies that the other particles that are in these blobs have to move as well. Therefore this result gives us a first indication that the dynamics of this system is not only heterogeneous, but also cooperative, qualitatively similar to results found in other glass-forming systems [11, 12, 13, 18, 28].

A further interesting observation is that if one considers the trajectory of a second tagged particle that, at $t = 0$ is within one of the blobs explored by the first particle, one finds that (generally) the former trajectory has a very strong overlap with the second one [29]. Thus it seems that there are lattice sites in the system that have a high throughput of particles whereas there are other sites in which there is no action, i.e. at these latter sites one finds for a very long time always the same particle (or, in rare exceptions, the same vacancy). Thus we can conclude that the relaxation dynamics of the system must be related to the presence of these sites with high traffic of particles. In order to investigate this point further we define a site as “active” if within the time interval $[0, t]$ it has been visited by more than one particle or vacancy. We emphasize that the presence of such active sites must be intimately related to the initial configuration of the particles, since, of course, on very long time scales all lattice sites must have exactly the same statistical properties (e.g. have had the same number of particles that passed through the site, etc.).

In Fig. 4 we show how the concentration of active sites $n_{act}(t)$, i.e. the total number of active sites divided by L^3 , depends on time and density. For short times $n_{act}(t)$ increases rapidly and we find $n_{act}(t) \approx \alpha(\rho)(1 - \exp(-t/\theta))$ with $\theta \approx 5$, independent of ρ , although the prefactor $\alpha(\rho)$ of this t -dependence decreases with ρ . This regime corresponds to the initial (fast) growth of the blobs, whose concentration decreases with ρ . Subsequently the shape of $n_{act}(t)$ depends strongly on ρ . For low densities the curves

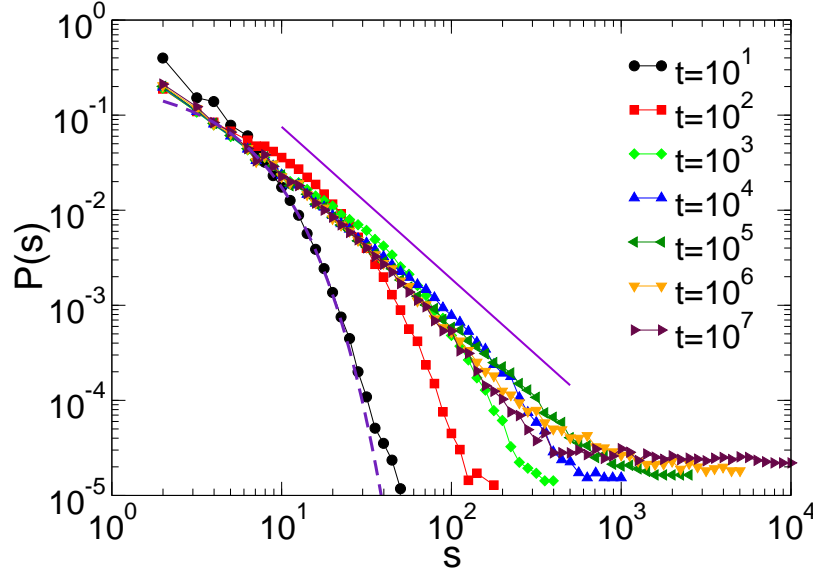


FIGURE 5. Distribution of cluster size, $P(s,t)$, where s is the size of cluster, for different times at density $\rho = 0.88$. Also shown (dashed line) is an exponential fit to $P(s,t)$ at $t = 10$ and (solid line) and the function $s^{-1.6}$ to demonstrate the emergence of power-law behavior of $P(s,t)$ at intermediate times.

approach rapidly $n_{act} = 1$, i.e. all the sites have seen more than one particle/vacancy, and thus the system has completely relaxed. This approach can be described well by a stretched exponential tail, with a stretching exponent of around 0.6, a functional form that is found also for the higher values of ρ . For high densities one finds a third regime in that $n_{act}(t)$ shows at intermediate times a very slow growth. This intermediate regime corresponds to the slow growth and coalescence of the blobs that will with time form the percolating structure seen in Fig. 3. Note that the growth rate of these blobs decreases rapidly with increasing ρ since the number of vacancies that are neighbors of the blob and which help it to grow decreases with increasing density. Also included in the figure is, for each density, the α -relaxation time τ_α (small arrows) which is defined as the time it takes for the intermediate scattering function to decay to e^{-1} . As we can see, τ_α corresponds to a time scale in which $n_{act}(t)$ has already entered the final stretched exponential decay, i.e. most of the sites have become active. Hence, the very slow growth at intermediate times seen at high ρ is not the α -relaxation of the whole system. However, it plays a significant role in the observed slowing down of dynamics prior to final relaxation.

In order to characterize the geometric structure formed by the active sites we have determined $P(s,t)$, the distribution of the size s of the clusters formed by these active sites at time t . (We define two active sites to belong to the same cluster if they can be connected to each other via a sequence of active sites that are nearest neighbors.) This distribution is shown in Fig. 5 for the (high) density $\rho = 0.88$. For short times $P(s,t)$ can be approximated well by an exponential distribution (dashed line) since at $t = 0$ the

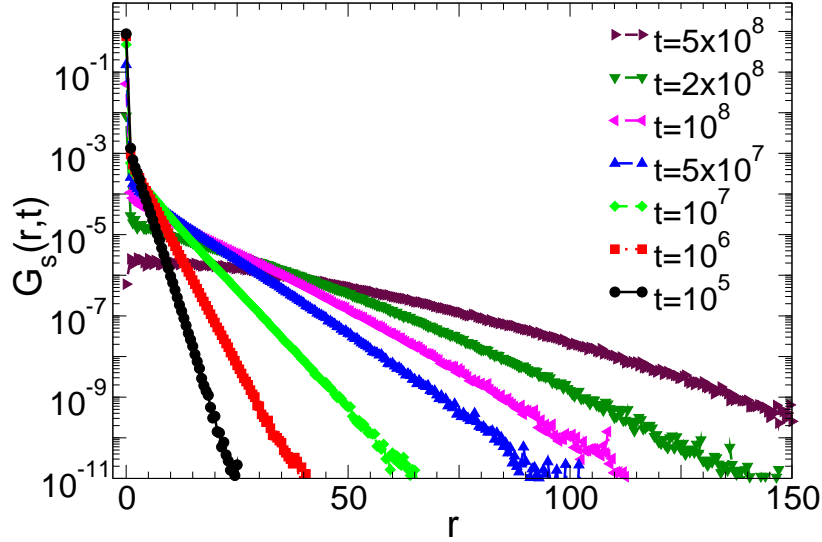


FIGURE 6. $G_s(r, t)$ for different times at a density of $\rho = 0.87$. The α -relaxation time at this density is $\tau_\alpha \approx 1.8 \times 10^7$.

active sites will be distributed randomly. With increasing t the geometric structure of the clusters starts to evolve towards a percolating backbone, i.e. the concentration of large clusters will grow. For intermediate times the distribution for small and intermediate s can be approximated well by a power-law, $P(s, t) \propto s^{-\nu}$, with a fractal exponent $\nu \approx 1.6$, which shows that the percolating structure has fractal nature. For very large s the distribution becomes flat, which is most likely a finite size effect related to the periodic boundary conditions. Note that the times shown in Fig. 5 are all significantly shorter than the α -relaxation time τ_α which, for this ρ , is around 4.4×10^8 . For times of the order of τ_α and beyond (not shown), the distribution $P(s, t)$ shows a peak at $s \approx L^3$, i.e. most of the sites in the system have become active.

Figures 3 and 5 show that the relaxation dynamics of the system is very heterogeneous in space and time. Thus it can be expected that there are certain particles that are relatively fast and others that are relatively slow. That this is indeed the case can be demonstrated by measuring the self part of the van Hove function $G_s(r, t)$ which is defined as [2]

$$G_s(r, t) = \frac{1}{N} \sum_{j=1}^N \langle \delta(r - |\mathbf{r}_j(t) - \mathbf{r}_j(0)|) \rangle \quad . \quad (2)$$

Thus $G_s(r, t)$ gives the probability that a particle makes within the time interval t a displacement of size r . In Fig. 6 we show this distribution function for $\rho = 0.87$. From this figure we recognize that for short and intermediate times the distribution has a strong peak at $r = 0$, i.e. most of the particles have not moved at all. Even for times as large as

$t = 10^5$ the fraction of particles that has moved a distance $r \geq 1$ is very small, only around 1%. If one looks at displacements $r \geq 1$ one finds that there are, e.g. for $t = 10^7$, even a few particles that have moved a distance as large as 50! Also noticeable is the fact that at intermediate times $G_s(r, t)$ is not given by a Gaussian distribution, as one would expect for a tracer particle that undergoes Brownian diffusion, but instead by an exponential distribution. Only for times that are much longer than the α -relaxation time, which at this density is around 1.7×10^7 , we find that $G_s(r, t)$ becomes a Gaussian, i.e. one has to go to very long time scales in order to observe a dynamics that is really random. From this figure we thus can conclude that those particles that can move already on time scales on the order of τ_α , do not seem to do this like a randomly diffusing particle. Instead the presence of the blobs, and at later time the percolating structure of the backbone, makes that the relaxation dynamics of these mobile particles obeys a different statistics. In the following section we will discuss this motion in more detail and also present a simple model that is able to describe it quantitatively. For the moment we thus just conclude that the relaxation of this simple glass-former happens in a hierarchical manner: First there is a fast local relaxation within blobs. Subsequently these blobs grow with a rate that depends strongly on density. The slow coalescence of these blobs lead to the formation of a percolating network. This backbone fattens until it finally occupies the whole lattice, which corresponds to the α -relaxation of the system. Hence we can conclude that the relaxation dynamics of this simple system does indeed show spacial and temporal heterogeneities, qualitatively similar to the ones that are (indirectly) observed in real glass-formers.

A CONTINUOUS TIME RANDOM WALK DESCRIPTION OF THE DYNAMICS

In this section we will present a simple model that is able to give a quantitative description of the relaxation dynamics, as described by the self part of the van Hove function, of glass-forming systems.

In order to have a model that is not only applicable to the lattice gas system discussed so far, we will consider a general glass-former, i.e. an off-lattice system. In a first step we thus have to understand the shape of the self part of the van Hove function for off-lattice systems. This function is shown in Fig. 7 for four different glass-formers. The data for silica, panel a), comes from a molecular dynamics simulation [30] with the so-called BKS-potential [31], an interaction potential that has been shown to reproduce many structural and dynamical properties of real silica [32, 33]. Panel b) shows data for a binary Lennard-Jones system [34], a model which in the past has been investigated intensively and has been found to share many properties of real simple glass-formers [35, 36]. The colloidal data shown in panel c) have been obtained by monitoring a colloidal suspension of hard sphere particles by means of a confocal microscope and which thus allows to track directly the trajectories of the particles [16]. Finally panel d) shows the data from a two-dimensional granular system in which the particles are shuffled horizontally via oscillating walls [37]. From this figure we can conclude that for all these glass-forming systems the distribution $G_s(r, t)$ shows a Gaussian central part and an exponential tail at larger distances. The only difference between these off-lattice systems

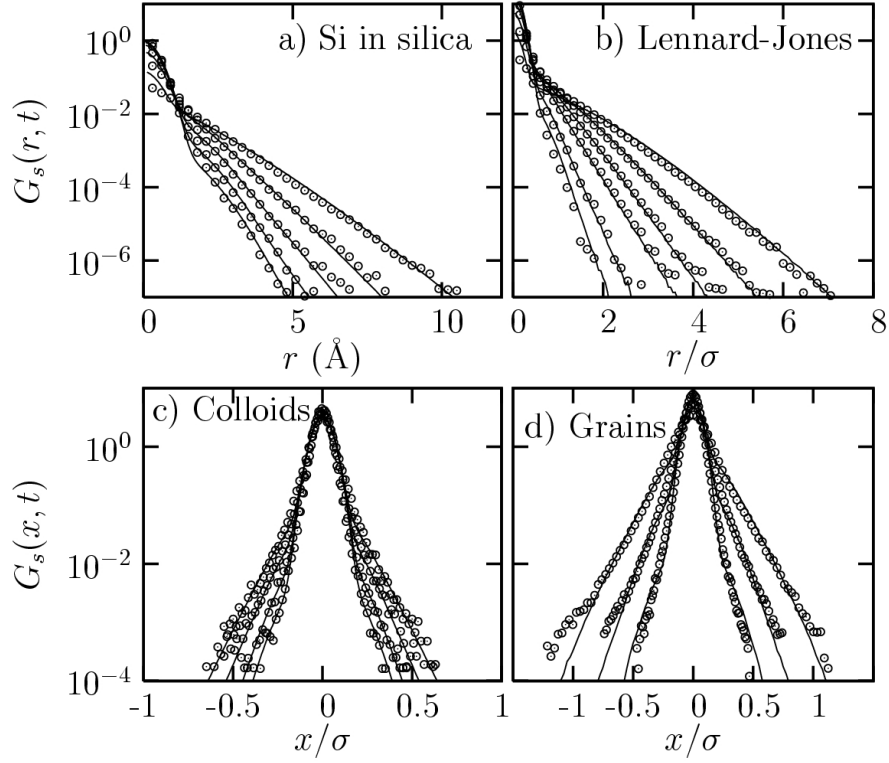


FIGURE 7. Self part of the van Hove function for different times and different systems. a) Silicon in a silica system. $T = 3000$ K and $t \in [27, 1650]$ ps. b) Lennard-Jones particles at $T = 0.435$ and $t \in [7.5 \times 10^4, 4.1 \times 10^7]$. c) Colloidal hard spheres at a packing fraction $\phi = 0.517$ and $t \in [90, 1008]$ s. d) A granular system at $\phi = 0.84$ and $t \in [10, 1000]$ cycles. a) and b) show the distribution of $|\vec{r}(t) - \vec{r}(0)|$, and c) and d) show the distribution of $x(t) - x(0)$.

and the lattice gas discussed above is thus that the latter system shows a δ -peak at $r = 0$ whereas in the former systems this peak is replaced by a Gaussian distribution. Similar results have also been found in other glass-forming systems [38, 39]. This finding is of course very reasonable, since in an off-lattice system the particles will, for short times, just oscillate around their (temporal) equilibrium position since they are trapped by their nearest neighbors. To a good approximation the local potential generated by the neighbors is given by a quadratic form, i.e. the oscillations of the particles is harmonic, which results in the observed Gaussian distribution of $G_s(r, t)$. No such harmonic oscillations are possible in a lattice system and thus the Gaussian is replaced by a δ -function.

In view of these findings for $G_s(r, t)$ we consider the following simple model for the dynamics of a tagged particle (similar ideas have been explored in Refs. [40, 41, 42, 43]). At early times the particle is locally trapped due to the presence of its neighbors. Hence it makes harmonic oscillations with a typical amplitude ℓ and which corresponds therefore to a Gaussian distribution of the displacement: $f_{\text{vib}}(r) = (2\pi\ell^2)^{-3/2} \exp(-r^2/2\ell^2)$. Thus if we start the clock at $t = 0$, at time t_1 the particle will have a displacement that is drawn from the distribution f_{vib} . At this time t_1 the particle makes a jump of length Δ and

we assume that the distribution of Δ is given by a Gaussian distribution of width d : $f_{\text{jump}}(\Delta) = (2\pi d^2)^{-3/2} \exp(-\Delta^2/2d^2)$. After this jump the particle will again vibrate harmonically around its new position and thus show a displacement that is distributed according to $f_{\text{vib}}(r)$. After a time t_2 it will make a new random hop by a distance that is given by the distribution $f_{\text{jump}}(\Delta)$. This alternation of vibrations and jumps gives us the relaxation dynamics of the particle. A model in which a particle makes an alternation between sitting/waiting and hopping is called continuous time random walk (CTRW) [44] and in the past it has been used to describe very different physical phenomena (hopping of atoms in semiconductors, flight of birds, etc.) [45].

Now, for any CTRW model, the distribution of the waiting times t_1 can be calculated from the one of t_2 [42]. However, for glass-forming liquids, these distributions of waiting times are very complex in nature, having significantly non-exponential shapes. It can be shown that, for such broad non-exponential distributions, $\langle t_1 \rangle \geq \langle t_2 \rangle$, where $\langle t_1 \rangle$ and $\langle t_2 \rangle$ are the first moments of the two distributions [46]. In the absence of any definite information regarding the shape of the distribution functions and also for simplifying calculations, we assume that the distributions ϕ_k for t_1 and t_2 are independent from each other and describe both of them with a single exponential, i.e. $\phi_k(t_k) = \tau_k^{-1} \exp(-t_k/\tau_k)$, with $k = 1, 2$. From such a dynamical model one can readily calculate the self part of the van Hove function and one finds [44]:

$$G_s(r, t) = \sum_{n=0}^{\infty} p(n, t) f(n, r) \quad . \quad (3)$$

Here $p(n, t)$ is the probability that the particle makes, within the time t , exactly n jumps and $f(n, r)$ is the probability that it makes in n jumps a displacement r . For the hopping dynamics of our CTRW model it is not difficult to carry out the sum in Eq. (3). If one goes into the Fourier-Laplace domain one finds

$$G_s(q, s) = f_{\text{vib}}(q) \Phi_1(s) + f(q) f_{\text{vib}}(q) \frac{\phi_1(s) \Phi_2(s)}{1 - \phi_2(s) f(q)} \quad , \quad (4)$$

where $\Phi_k := (1 - \phi_k(s))/s$ and $f(q) := f_{\text{vib}}(q) f_{\text{jump}}(q)$. (We mention that Eq. (4) is valid for any choice of distribution ($f_{\text{vib}}, f_{\text{jump}}, \phi_1, \phi_2$), i.e. is not restricted to the exponential and Gaussian distributions considered here.) Using the four free parameters ℓ, d, τ_1 , and τ_2 as fit parameters, we have used the expression (4) to fit the data shown in Fig. 7. Note that i) a given choice of fit parameter must allow to fit the data for *all* the times considered and ii) that the inverse-Fourier transforms have to be done numerically. The resulting fits are included in the figure as well (solid lines) and we see that the agreement is indeed very good. Hence we can conclude that, despite the simplicity of the model, it is able to capture some of the characteristic of the relaxation dynamics of a tagged particle in a glass-forming system. It is also of interest to mention that the values for ℓ and d that result from the fits are very reasonable. To a good approximation we find $d \approx 2\ell$ and $(d/\sigma, \ell/\sigma)$ is (0.1, 0.051) for colloids, (0.15, 0.06) for grains, and (0.35, 0.15) for the Lennard-Jones system. Moreover, our results for d^2 agree well with the height of the plateau measured in the mean-squared displacements for all systems. Hence we can conclude that the parameters of the model have values that are physically very reasonable.

Finally we discuss the origin of the exponential tail in the distribution function $G_s(r, t)$. For simplicity we consider the special case that $\ell = 0$, i.e. no vibrational motion occurs, and $\tau_1 = \tau_2$. For this choice one obtains the analytic result

$$G_s(r, t) = G_0 + \frac{4\pi e^{-t/\tau_1}}{r} \int_0^\infty dq [e^{tf(q)/\tau_1} - 1] q \sin(qr) \quad , \quad (5)$$

where $G_0(r, t) \equiv \delta(r)\Phi_1(t)$. By expanding the exponential in Eq. (5) in a power series, integrating each term and converting the resulting sum into an integral one obtains

$$G_s(r, t) = G_0(r, t) + \frac{\pi e^{-t/\tau_1}}{4d^3} \int_1^\infty dn \frac{e^{-f(n)}}{n^2} \quad , \quad (6)$$

with $f(n) := n \ln n - n \ln(t/\tau_1) - n + r^2/(8d^2n)$. For large r , Eq. (6) can be evaluated using a saddle point approximation and then gives

$$G_s(r, t) \sim \frac{(\pi Y)^{3/2} e^{-t/\tau_1}}{(rd)^{3/2} \sqrt{1+Y^2}} e^{-r[Y-1/Y]/2d} \quad , \quad (7)$$

where Y is defined via the equation $Y^2 \exp Y^2 = r^2/(2dt/\tau_1)^2$, i.e. $Y^2 \sim 2 \ln(r^2/(2dt/\tau_1))$ if r is large. Thus we find that $G_s(r, t)$ has for large r indeed an exponential tail (with logarithmic corrections), as found in the simulation and experimental data (see Fig. 7). We emphasize that the asymptotic result given by Eq. (7) can be obtained for any distribution of $f_{\text{vib}}(r), f_{\text{jump}}, \phi_1, \phi_2(t_2)$, i.e. it is a quite general result. The exponential tail is thus a direct consequence of the fact that the timescales between the jumps is a distributed quantity and so it directly follows from the dynamically heterogeneous behavior observed in glass-formers.

CONCLUSIONS

In this paper we have discussed the relaxation dynamics of a lattice gas model in which the only non-trivial features are the rules governing the motion of the particles. Despite its simplicity, this model has a dynamics that is similar to the one of real glass-forming systems in that it shows a strong slowing down with increasing density and a stretching of time correlation functions. By tracking the trajectory of a tagged particle, we found that its dynamics is very heterogeneous in space and time, in agreement with the dynamics of real glass-formers, for which, however, the existence of dynamical heterogeneity can usually be inferred from experimental data only in an indirect way. We find that the regions in which the particles move form, at early stages, isolated blobs, which, with increasing t , grow and start to percolate. The resulting spanning structure allows some of the particles to make relatively quickly large displacements, a behavior that gives rise to an exponential tail in the self part of the van Hove function. At very large times, i.e. much larger than the α -relaxation time, the cluster of active sites fills the whole space and thus the system has completely relaxed.

Although not discussed in the present manuscript, it is possible to predict to some extent at which lattice sites the blobs and the percolating cluster will occur. In Ref. [29]

it was shown that these active sites are strongly correlated with lattice sites that have, at time $t = 0$, a relatively low local density of particles. Hence we can conclude that, for this model, the initial configuration of the particles allows to predict the details of the relaxation dynamics of the system at short and intermediate times.

Finally we have shown that the exponential tail of the van Hove function can be rationalized by a simple model based on a continuous time random walk and that this model can be used successfully to describe also the space and time dependence of $G_s(r, t)$ for off-lattice models. Since at the moment this model is purely phenomenological, it will be interesting to see whether it is possible to derive it from a more microscopic many-body theory such as mode-coupling theory [4, 5, 7]. Last but not least it is also important to investigate better to what extent the percolating cluster that we find to be important for the relaxation dynamics of the lattice gas discussed here, is present also in off-lattice system. Thus it is evident that despite the present results, there are still many open and interesting questions regarding the relaxation dynamics of glass-forming systems.

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